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Optimal H_2O_2 Concentration in Advanced Oxidation over Titanium Dioxide Photocatalyst

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The oxidative degradation of Rhodamine B dye under ultraviolet irradiation was studied. The degradation rate was measured with using of smartphone camera. Photocatalytic degradation of the Rhodamine B dye over the P25-TiO_2 catalyst has been found to accelerate substantially in the presence of hydrogen peroxide. The relationship between the photocatalytic degradation rate and H_2O_2 concentration has been studied. The optimal concentration of H_2O_2 has been found to in the range of 10 - 25 mM. The proposed mixture of P25 photocatalyst and H_2O_2 oxidizer can be used to remove organic pollutions from industrial waste water.

Key words: photocatalyst; titania; hydroxyl radicals; Rhodamine B; wastewater remediation.
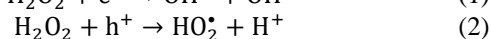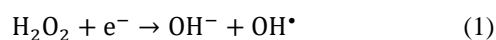
Introduction

Titanium dioxide with crystalline anatase modification is well-known as a photocatalyst [1, 2]. The advantages of titanium dioxide are the following: high photocatalytic activity, chemical and thermal stability, low cost and negligible toxicity [2, 3]. The photocatalytic activity is a result of favorable band gap in electronic structure of TiO_2 semiconductor crystals [4]. Upon the absorption of a light quantum, an electron-hole pair is formed. The free electron (e^-) and hole (h^+) can migrate in the crystal lattice: $TiO_2 + h\nu \rightarrow TiO_2$ ($e^- + h^+$). The charge carriers trapped by TiO_2 surface are extremely reactive. Almost any organic compounds can be photooxidized on TiO_2 surface to CO_2 and H_2O [2, 5-8]. Viruses and bacteria can be destroyed over the photocatalytic surface as well [9-12].

The main oxidative species in the photocatalytic reactions are hydroxyl ($\bullet OH$) and hydroperoxyl ($\bullet OOH$) radicals. Rate of the heterogeneous photocatalytic oxidation depends on TiO_2 polymorph used (anatase, rutile, brookite), specific surface area of the photocatalyst, intensity and wavelength of UV-irradiation as well as solution pH. Under normal conditions, the thermodynamically stable phase of titanium dioxide is rutile. Both anatase and brookite polymorphs are thermodynamically metastable and can transform to rutile under the heat treatment.

Hydrogen peroxide H_2O_2 is a convenient and environmentally friendly oxidizer. The advantages of H_2O_2 as compared with other oxidizers for wastewater treatment are lack of harmful by-products and satisfactory stability. In contrast to compressed chlorine gas, H_2O_2 dosing does not require complex equipment. Moreover, small residual concentration of hydrogen peroxide promotes processes of aerobic biological treatment. For that reason, H_2O_2 is the promising oxidizer for use in Advanced Oxidation Processes (AOPs) [13, 14]. The efficiency of hydrogen peroxide in AOPs is determined by concentration of radicals formed. Under UV-light irradiation, hydrogen hydroxide molecule decomposes with the formation of two hydroxyl radicals. H_2O_2 decomposition is catalyzed also with transition metal ions. The well known example is co-called Fenton catalyst (Fe^{2+} ions). Mechanism of photo-catalytic decomposition of H_2O_2 is more complex. Free charge carriers on the irradiated photocatalyst surface lead to reduction and oxidation of hydrogen peroxide:

$$H_2O_2 + e^- \rightarrow OH^- + OH^\bullet \qquad (1)$$
$$H_2O_2 + h^+ \rightarrow HO_2^\bullet + H^+ \qquad (2)$$

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As a result, the very reactive hydroxyl HO$^{\bullet}$ and hydro-peroxide HO$_2^{\bullet}$ radicals are formed. Rutile surface promotes mainly reduction of H_2O_2 (the reaction 1) while anatase surface promotes mainly oxidation of H_2O_2 (reaction 2) [15]. In other words, the rutile form of titania has rather reducing properties and the anatase form has rather oxidizing properties [16, 17]. To date, the details of photocatalytic decomposition of H_2O_2 remain unclear [15]. Upon addition of hydrogen peroxide, hydroxyl radicals are generated due to H_2O_2 reduction by electrons from the conduction band of rutile [18, 19]. As a result, the overall rate of photodegradation reaction significantly increases [20, 21]. In the case of anatase, the overall photodegradation rate is slightly lesser [22]. Optimal amounts of H_2O_2 and photocatalyst depend on titania type and specific surface, photoreactor geometry, light intensity as well as pollutant type and concentration [6, 14, 23-29].

The aim of this study was to evaluate optimal dosage of hydrogen peroxide to increase photocatalytic degradation rate. The Rhodamine B (RhB) dye was used as model pollutant. The impact of different concentration of hydrogen peroxide on photocatalytic activity of the P25 titania was studied depending on time, initial RhB concentration and photocatalyst loading.

I. Materials and methods

1.1. Materials

The commercial titania photocatalyst Aeroxide TiO$_2$ P25 was obtained from Evonik. It contains 80 % anatase and 20 % rutile with the average particle size of 30 nm. The average BET surface area was approximately 50 m^2/g. The P25 photocatalyst is often used as a reference material [6]. The Rhodamine B dye ($\geq$ 95 %) and H_2O_2 (31.5 %) were obtained from Merck.

1.2. Dye photodegradation tests

The micro photoreactor and the experimental details were described in the foregoing paper [30]. An exact mass (10, 20, 30 and 40 mg) of TiO$_2$-P25 photocatalyst was placed in the microreactor with 20 ml of aqueous solution of RhB (5; 25 and 100 mg/L). The suspension was magnetically stirred in the dark for 40 min to attain adsorption equilibrium. The irradiation source was a 3W LED with λ = 365 nm. The duration of photodegradation was 30 min. An aliquot of studied dye solution was taken, the photocatalyst was separated by centrifugation at 4000 rpm, and the optical density was measured by UV-Vis spectrophotometer ULAB 102-UV at 560 nm. Kinetic lines were registered with using the smartphone Samsung Galaxy A6 (SM-A600FN) 3/64Gb. The details of the color measurements have been described in the recent paper [31].

II. Results and discussion

2.1. Effect of H_2O_2 concentration

The addition of H_2O_2 to reaction mixture results in acceleration of the RhB dye degradation (Figs. 1 and 2). The obvious reason is formation of highly reactive hydroxyl radicals. An increase in the H_2O_2 concentration resulted in decrease of final RhB amount. The decrease was 2.5 times in the case of initial RhB concentration equal to 100 mg/L. In the case of initial RhB concentration equal to 25 mg/L, almost complete photodegradation of RhB is achieved with 10 - 25 mM H_2O_2 (Fig. 1b). All the numerical data on degree of RhB degradation are summarized in Fig. 3.

Figure 3 indicates clearly that effective concentration of H_2O_2 depends on initial concentration of the model pollutant. For example, concentration of H_2O_2 has no marked effect at RhB concentration equal to 5 mg/L. Photocatalyst alone generates radicals enough for deep degradation of the dye. UV-irradiation for both 30 min and 45 enables quite high degradation extent. At RhB concentration equal to 25 mg/L, addition of H_2O_2 results in increase of the degradation extent from 42.59 % to
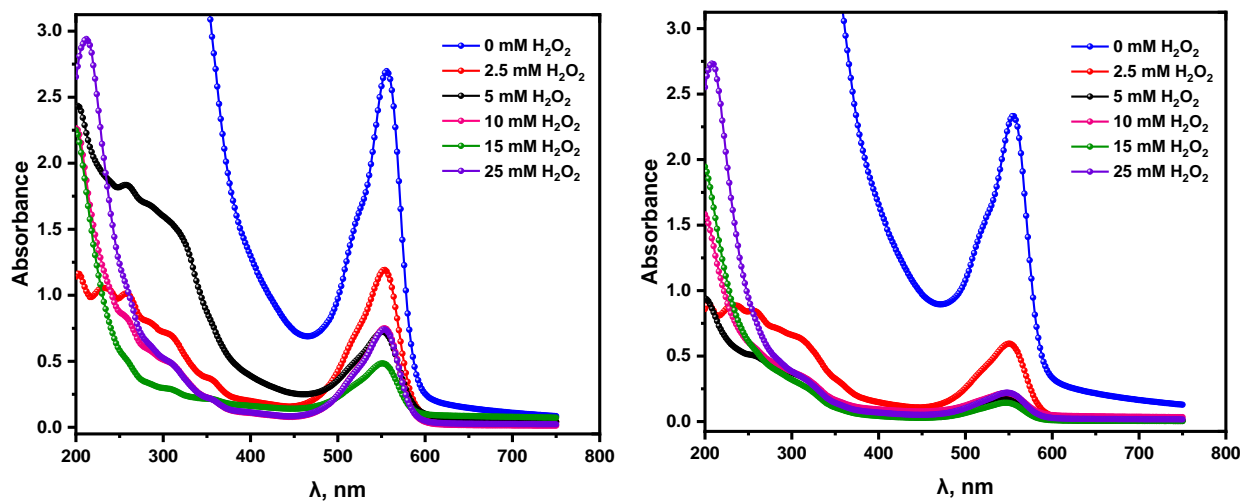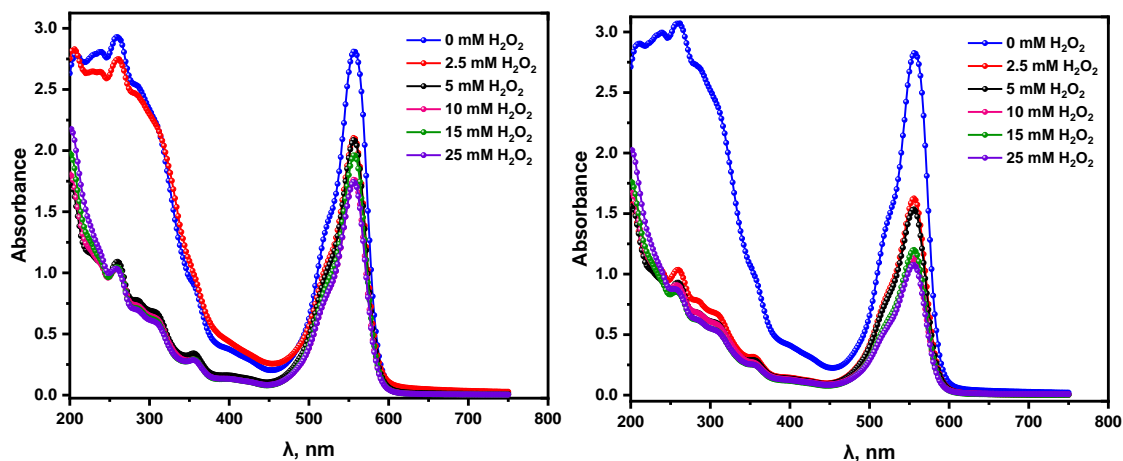

Fig. 1. UV-vis spectra of Rhodamine B dye solutions after UV irradiation for 30 min (a) and 45 min (b) at indicated concentrations of hydrogen peroxide. The experimental conditions are the following: m(TiO$_2$) = 30 mg, V(solution) = 20 mL, C(RhB) = 25 mg/L.

Fig. 2. UV-vis spectra of Rhodamine B dye solutions after UV irradiation for 30 min (a) and 45 min (b) at indicated concentrations of hydrogen peroxide. The experimental conditions are the following: m(TiO_2) = 30 mg, V(solution) = 20 mL, C (RhB) = 100 mg/L.
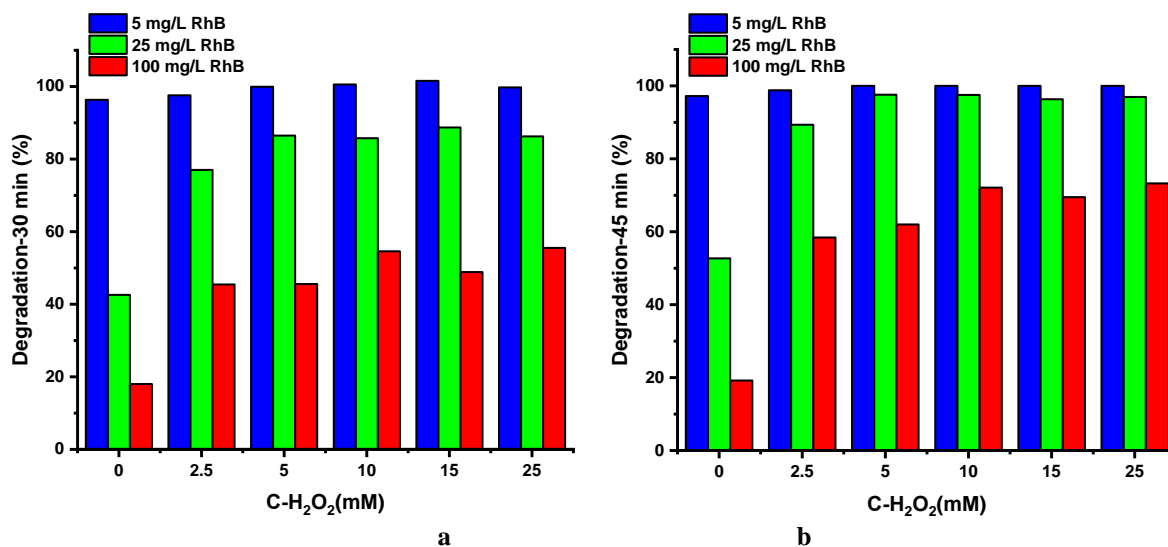

Fig. 3. Degradation efficiency of RhB with different amounts of H_2O_2 after UV irradiation for 30 min (a) and 45 min (b).

77.04 % (at 2.5 mM H_2O_2) (Fig. 3a and Fig. 3b respectively). Maximal degradation extent is 97.59 % at 10 mM H_2O_2 after 45 min of UV-irradiation. At RhB concentration equal to 100 mg/L, the addition of H_2O_2 has substantial effect (Fig. 3). The degradation extent increased from 18.0 % (at 0.0 mM H_2O_2) to 45.44 % (at 2.5 mM H_2O_2). Maximal degradation extent is 73.26 % at 25 mM H_2O_2 after 45 min of UV-irradiation (Fig. 3b).

2.2. Effect of catalyst dosage

Fig. 4 shows the experimental spectra of the RhB solutions UV-irradiated at different doses of the titania photocatalyst and at constant concentration (5 mM) of hydrogen peroxide. It can be seen that the higher TiO_2 dose the deeper degradation of the RhB dye.

Fig. 5 shows corresponding percentages of degradation extent. With adding titania photocatalyst, the degradation extent is increased from 2 % (at zero titania) to around 77 % (at 10 mg TiO_2). This substantial effect is due to hydroxyl radicals generated by TiO_2 surface. Further increase in photocatalyst dosage results in increase of degradation extent to 88 % (at 20 mg TiO_2)
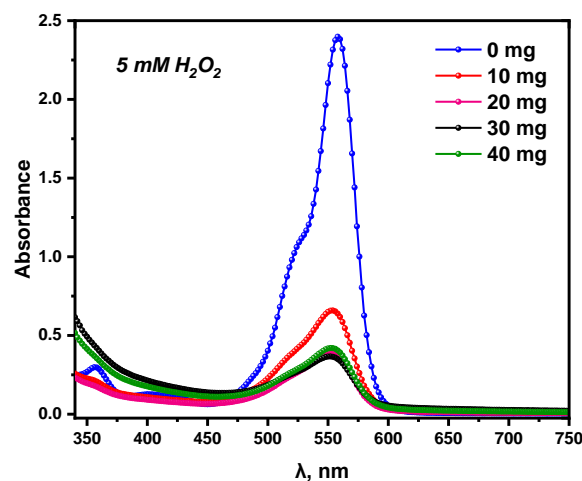

Fig. 4. UV-vis spectra of Rhodamine B solutions after UV irradiation for 30 min at indicated TiO_2 dosages (conditions: V(solution) = 20 mL, C(RhB) = 25 mg/L, C(H_2O_2) = 5mM).
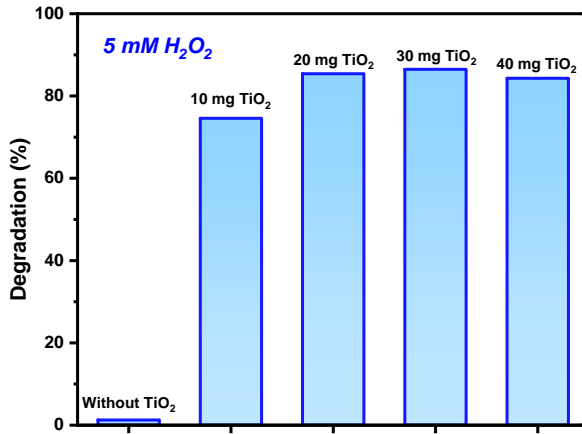
Fig. 5. Degree of Rhodamine B degradation after UV irradiation for 30 min at indicated TiO$_2$ dosages. The experimental conditions are the following: V(solution) = 20 mL, C(RhB) = 25 mg/L, C(H$_2$O$_2$) = = 5mM.

and 89 % (at 30 mg TiO$_2$). Further increase of TiO$_2$ amount to 40 mg leads to decrease in degradation extent to 86 %. The most probable cause is optical shielding of reactor volume by excessive amount of TiO$_2$ suspension. It can be concluded that optimal dose of TiO$_2$ is equal 30 mg.

2.3. Effect of Rhodamine dye concentration

The RhB dye solutions of different concentrations (5, 25 and 100 mg/L) reveal different degradation extents for 30 min (Fig. 6a-e). The highest degradation extent is observed at initial RhB concentration equal to 5 mg/L. The solutions with initial RhB concentration 25 mg/L reveal moderate degradation. The solutions with initial RhB concentration 100 mg/L reveal the lowest degradation. The obvious reason is the difference of RhB amounts to degrade. The dye degradation is deeper after 45 min.

2.4. Smartphone-based measurements

Kinetic measurements of the RhB photodegradation was performed with using smartphone camera. Smartphone-based measurements provide fast results to
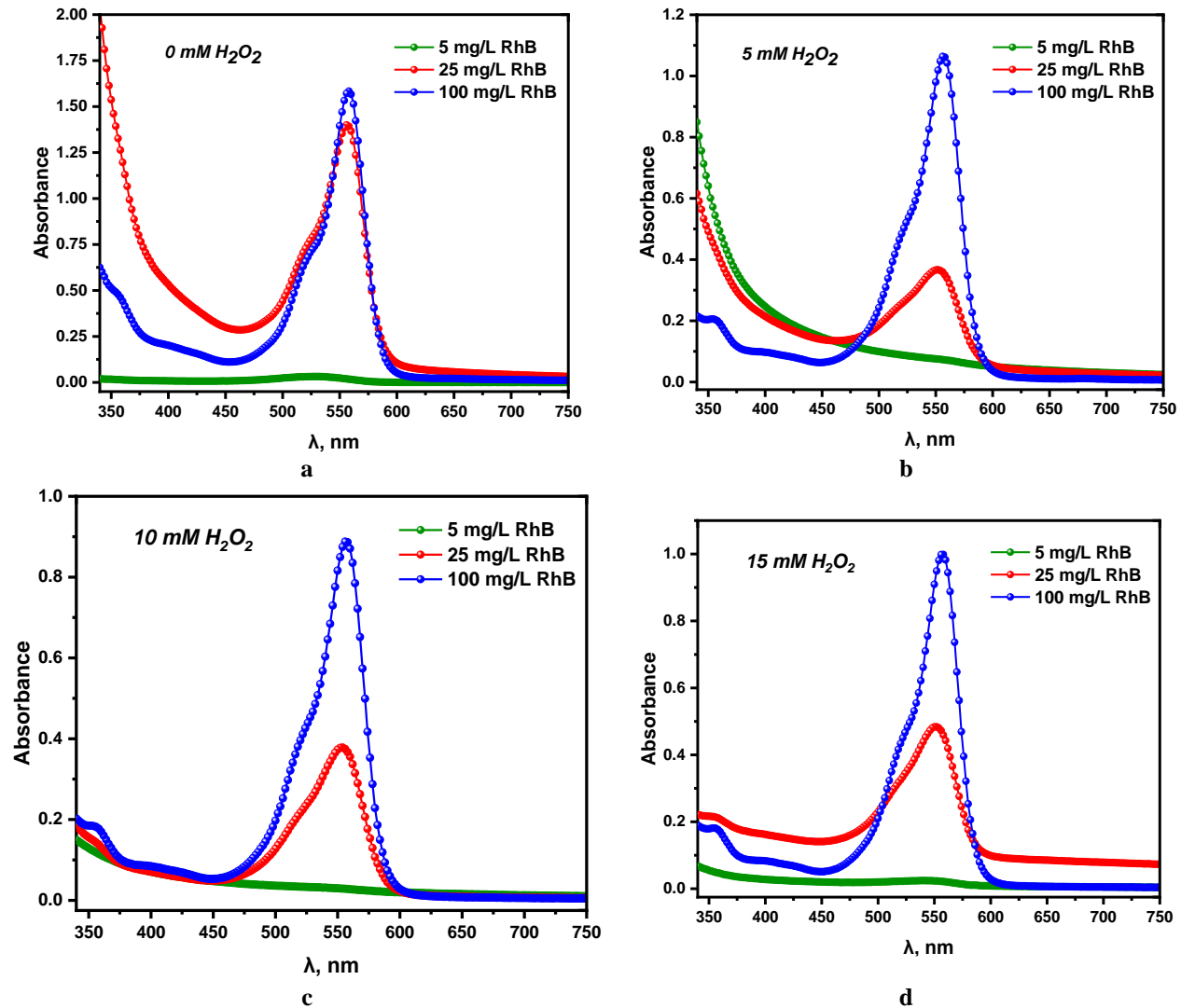

Fig. 6. UV-vis spectra of Rhodamine B solutions after UV irradiation for 30 min at indicated concentrations of RhB and H$_2$O$_2$. The experimental conditions are the following: m(TiO$_2$) = 30 mg, V(solution) = 20 mL.
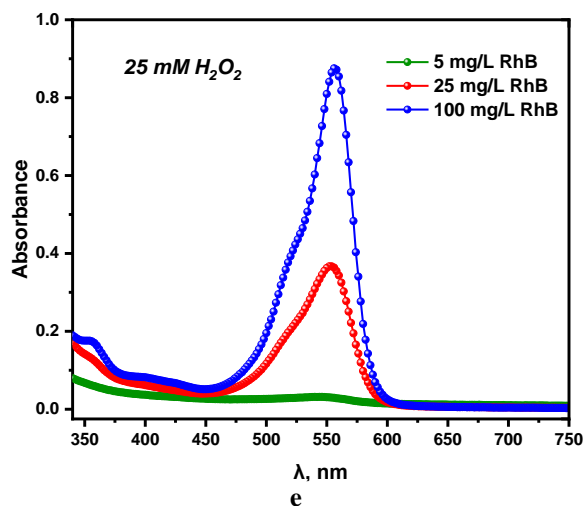
Fig. 6e. UV-vis spectra of Rhodamine B solutions after UV irradiation for 30 min at indicated concentrations of RhB and H_2O_2. The experimental conditions are the following: $m(TiO_2) = 30$ mg, V(solution) = 20 mL.
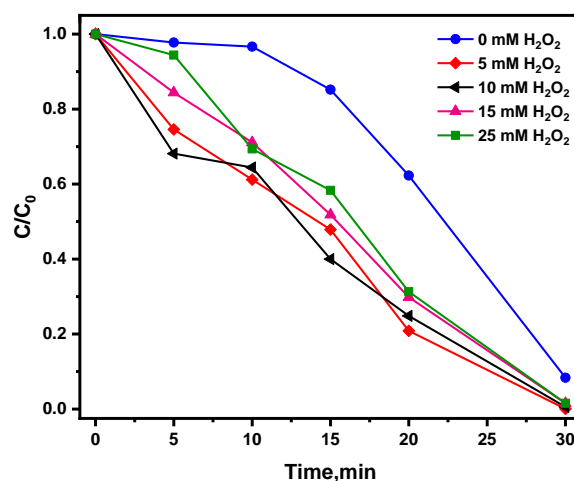

Fig. 7. Kinetic lines of the RhB dye photodegradation at initial concentrations 5 mg/L and indicated concentrations of H_2O_2. The experimental conditions are the following: V(solution) = 20 mL, $m(TiO_2) = 30$ mg.

Table 1

Examples of H_2O_2 use for the photocatalytic degradation of organic pollutants

Pollutant	Photocatalyst	Pollutant concentration	Optimum catalyst dose	H_2O_2 concentration	Degradation extent, %	Ref.
Reactive Red-147	TiO_2	50 mg/L	0.60 g/L	7.92 mM	92.0	[24]
Methylene blue	Cr/CeO_2	10 mg/L	0.40 g/L	0.35 mM	59.0	[25]
Methylene blue	TiO_2	200 mg/L	0.20 g/L	146.6 mM	99.0	[23]
Methylene blue	1D-Cu	40 mg/L	2.00 g/L	44.0 mM	84.9	[27]
terbuthylazine	TiO_2-Fe^{3+}	7.0 mg/L	0.10 g/L	1.32 mM	100.0	[26]
2-nitrophenol	Ag-S/PEG/TiO_2	50 mg/L	0.545 g/L	316 mM	88.6	[14]
Rhodamine B	P25-TiO_2	5.0 mg/L 25 mg/L 100 mg/L	1.50 g/L	5.00 mM 10.0 mM 25.0 mM	100.0 97.5 73.2	This work

estimate the dye degradation kinetics. One more advantage is that RGB color measurements do not require sampling. In such a way, volume of the reaction mixture remains constant. The obtained kinetic lines are presented in Fig. 7.

Fig. 7 indicate clearly substantial effect of H_2O_2 on the photodegradation kinetics. The higher the H_2O_2 concentration, the deeper is the degradation of RhB dye. At low concentration of RhB (5 mg/L), the kinetic lines are is almost linear (Fig. 7). The maximal photodegradation rates are observed at H_2O_2 concentration equal to 10 mM. The probable reason of slower degradation rate at higher H_2O_2 concentrations may be side reaction. The formed hydroxyl radicals may react with excessive amount of H_2O_2 resulting in less reactive species. The examples of photocatalyst and H_2O_2 use for the photocatalytic degradation of different organic pollutants are summarized in Table 1. It can be concluded that the presence of hydrogen peroxide leads to the increase in the photocatalyst activity and enhance the photocatalytic processes in few times.

Conclusion

Photocatalytic oxidation, enhanced with hydrogen peroxide, provides complete degradation of the Rhodamine B dye for several tens of minutes. Effects of reaction parameters were studied. Increase of reaction time results in deeper degradation. Increase of dye concentration results in decrease of the degradation extent. Both the effects are rather obvious. In turn, hydrogen peroxide concentration has non-monotonic effect. With addition of H_2O_2, the degradation extent is increased as compared with the oxidation in the presence of the single photocatalyst. Increase in H_2O_2 concentration above 15 mM results in decrease of photocatalytic oxidation rate. Probably, the excessive amount of H_2O_2 may promote side reaction(s).

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Оптимальна концентрація H$_2$O$_2$ для процесів глибокого окиснення на фотокаталізаторі TiO$_2$

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Досліджено фотокаталітичне окиснення барвника Родаміну В під дією ультрафіолетового опромінення. Швидкість деградації виміряно за допомогою камери смартфону. Встановлено, що фотокаталітична деградація барвника Родаміну В каталізатором P25-TiO$_2$ значно прискорюється у присутності пероксиду водню. Вивчено взаємозв'язок між швидкістю фотокаталітичної деградації та оптимальною концентрацією H$_2$O$_2$. Встановлено, що оптимальна концентрація H$_2$O$_2$ знаходиться в діапазоні 10 - 25 ммоль/л. Активація фотокаталізатора P25 в присутності окисника H$_2$O$_2$ може бути використана для видалення органічних забруднень з промислових стічних вод.

Ключові слова: фотокаталізатор; титан (IV) оксид; гідроксильні радикали; Родамін В; очистка стічних вод.